Chapter 5

Bioactive Compounds in Pigmented Maize

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Additional information is available at the end of the chapter

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Abstract

Mexico is the center of origin of maize where there is a great variety of pigmented corns with health benefits. These properties are attributed to their high content of phenolic compounds. The most studied compounds are anthocyanins that no matter the variety of corn are mainly six: cyanidin, pelargonidin and peonidin-3-glucoside and their malonated derivatives. Among the pigmented corns, the purple has the most concentration of anthocyanins, these are found in the whole plant but in more quantity in the silk. The health benefits attach to anthocyanins are principally anti-obesity agent and anticancer activity. Regarding the phenolic acids reported in the pigmented corn plant, the most abundant acid in kernel is ferulic acid, in cob is syringic acid while in the silk is chlorogenic acid. This variation, in the phenolic acid profiles according to the organ, indicates the biological function that each of them plays in the plant; meanwhile in humans, they have important antioxidant effects. Flavonoids are the group less studied of bioactive compounds in pigmented corns; however, the concentrations of these compounds are high especially in purple silk; inside the flavonoids described are morin, kaempferol, naringin, maysin, rutin, quercetin and hyperoside; with antioxidant effects, as neuroprotective, apoptosis induction and others.

Keywords: pigmented corn, anthocyanins, flavonoids, phenolic acids

1. Introduction

The oldest macroremains unambiguously identified as maize (*Zea mays*) were retrieved from preceramic strata of dry caves in two states of Mexico: Puebla (Tehuacan Valley) and Tamaulipas (Ocampo Caves). These were found with microremains of pepper (*Capsicum*) and squash (*Cucurbit asp)* and other species used by humans. Archeological strata, suggesting a rough date for this foods around 9000–7000 B.P. [1]. In different myths, leyends and codices prehispanics civilizations Olmecas, Mayan and Mexican showing the prominent position of corn. For example, one myth the Mexica gods of corn: Tell us that corn was created after the goddess Centéotl sank into the ground to make vegetables to feed the people. It was in the wake of that event that cotton, huazantle, chia, sweet potato and corn began to grow from the ground. The Mexican Indians called corn as "the plant of the gods" [2].

At this time, corn (*Zea mays*) is the most important cereal that is produced in the world, the white and yellow corns are more used, the world production of maize was 987 million metric tons (MMT) and the United States of America (USA) is the largest producer and Mexico is the sixth producing country [3].

In the world, corn is generally used for animal feed and biofuels. In Mexico, this cereal is used for making foods; maize grains are consumed fresh (elotes and esquites, boiled grains) or processed in the form of dough or cornmeal for the preparation of some foods: dishes (tortillas), corn flakes (salads and sweets totopos), starch (atoles and pinole), tamale dough (tamales), fermented foods (pozol and atoles), boiled or steamed corn (pozole), soups (chilaquiles), bakery products and another foods. Some foods and grains of maizes are depicted in **Figure 1**.

The colorful corns are less common while the white and yellow are the most popular. All parts such as silk, cob, leaves, husk and kernel of corns have been used by people at remote time to Mesoamerican civilization, the pigment corns referred to as blue, red or purple corn are botanically the same species white and yellow. This cereal was used in the preparation to color foods and beverages. The interest on pigmented (blue, red and purple) corn is due to the bioactive compounds; these are anthocyanins, *p*-hydroxycinnamic acids, flavonoids and to minor proportion carotenoids, phytoesterols, vitamin E, lignans, policosanols and xylans. The purpose of this chapter is to provide an overview of bioactive compounds and of the

Figure 1. Food products elaborated with pigmented corn.

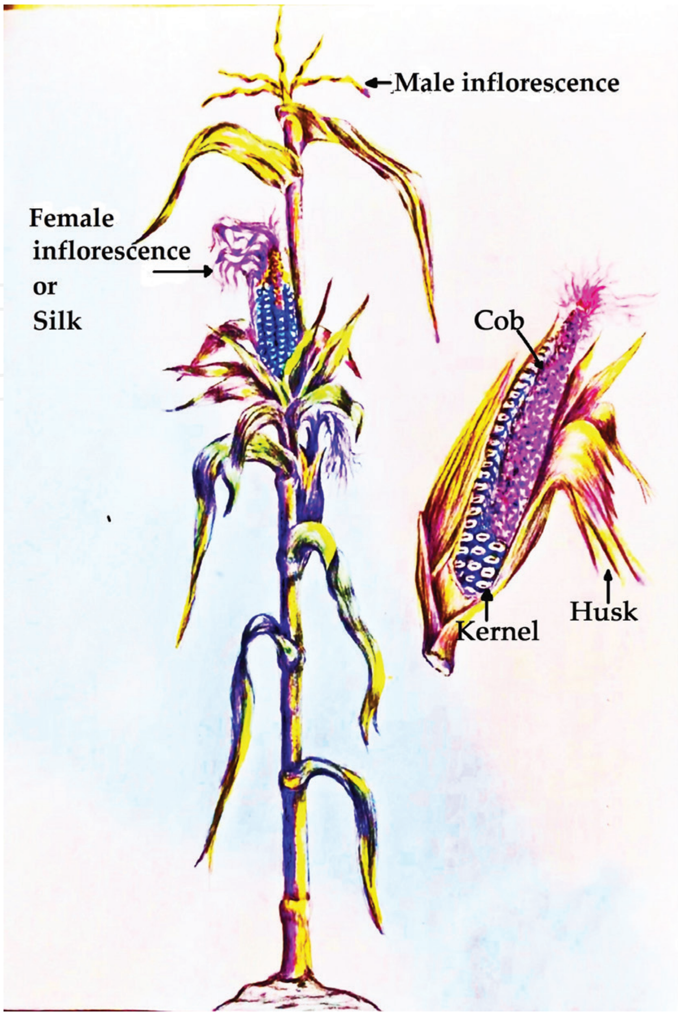

Figure 2. Organs of the corn plant. Painting by Esteban Torres 2018.

biological activity of the purple, red and blue corns in all parts of the plant including pericarp of the grain (kernel), silk (seda), inflorescence (espiga), husk (totomoxtle) and corn cobs (olote). The plant parts typical to corn are shown in **Figure 2**.

2. Anthocyanin in pigmented corn

Anthocyanins are the largest group of phenolic pigments responsible for the pink, red, purple and blue corns which is the cereal with most anthocyanin content [4]. For that reason, the pigmented corn has caught attention in research and production. There is a great diversity in types of corn including sweet corn, popcorn, pod corn, flint corn, flour corn, waxy corn and dent corn; everyone is able to have different variety of color as shown in **Figure 3**, which give us opportunity to get a great source of anthocyanins using the whole plant because, according with the variety of corn, the silk, corn husk and corn cob could have more anthocyanins than kernel, as we will see in later section.

Figure 3. Purple corn and Cacahuacintle corn with purple cornhusk and corn cob.

2.1. Anthocyanin in pigmented corn kernel

Anthocyanin in corn is found in kernel, cob, husk, silk, leaves and stem [5, 6]. In terms of anthocyanins, kernel is the most studied and anthocyanins are found in pericarp and aleurone layer. Pericarp can be transparent, orange, red or brown while aleurone layer can be transparent, red or purple [7]. Currently, researches in corn are focused on major production of anthocyanins, so there are some strategies to find new and better source of pigmented corns. One of them is the study of Mexican maize due to an excellent source for the production of anthocyanins because there are more than 60 native races of corn that have been little studied. However, Mendoza had studied the anthocyanins content in different corn lines and found corns with higher anthocyanins [8]. Other strategy is hybrid corn which is also studied; nevertheless, the anthocyanins content is not better than other pigmented native corns.

The later research about anthocyanin characterization shows a similar profile include cyanidin-3-glucoside and cyanidin-3-(6″malonyl) glucoside as the main anthocyanins. **Figure 4** shows anthocyanins found in pigmented corn. However, the variety of colors on pigmented corns is due to the difference on the concentration of each anthocyanin depending on genetics [9]. Peonidin-3-glucoside and pelargonidin-3-glucoside and their derivatives are the anthocyanins that have major variability and a major concentration of pelargonidin-3-(6″malonyl) glucoside are found in red corn [10] while blue corn has neither pelargonidin-3-glucoside nor peonidin-3-glucoside as purple corn has [11], moreover blue corn has more cyanidin-3-(6″ malonyl)glucoside than purple corn; however, its total concentration is much less than purple corn as shown in **Table 1** [9].

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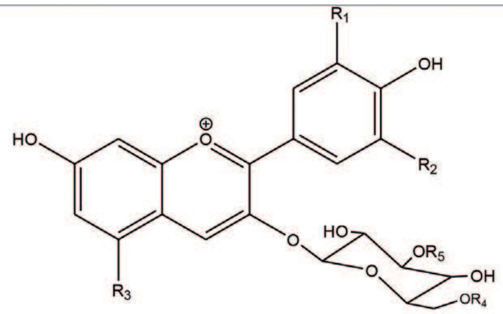


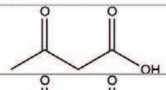
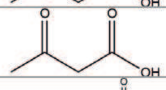
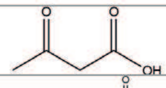
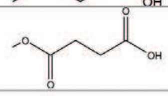
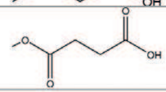
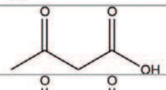
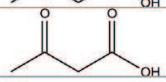
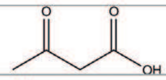
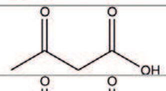
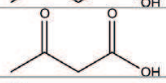
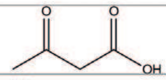
Anthocyanin	R1	R2	R3	R4	R5
Cyanidin-3-glucoside	OH	H	H	H	H
Cyanidin-3,5-diglucoside	OH	H	Glucose	H	H
Cyanidin-3-(6″malonyl)glucoside	OH	H	H		H
Cyanidin-3-(3″,6″dimalonyl)glucoside	OH	H	H		
Cyanidin-(disuccinyl)glucoside	OH	H	H		
Pelargonidin-3-glucoside	H	H	H	H	H
Pelargonidin-3,5-diglucoside	H	H	Glucose	H	H
Pelargonidin-3-(6″malonyl)glucoside	H	H	H		H
Pelargonidin-3-(dimalonyl)glucoside	H	H	H		
Peonidin-3-glucoside	OCH_3	H	H	H	H
Peonidin-3-(6″malonyl)glucoside	OCH_3	H	H		H
Peonidin-3-(dimalonyl)glucoside	OCH_3	H	H		
Delphinidin-3-glucoside	OH	OH	H	H	H

Figure 4. Structure of anthocyanin found in pigmented corn.

2.2. Anthocyanin in pigmented corn cob

Cob is considered as a by-product from the corn and represents the 20.6–26.2% of the plant and it is used as animal feed. However, it has a chemical high value due to their high anthocyanin concentration and other phenolic compounds. Purple corn cob anthocyanin concentration is 3–3900 mg/100 g according to the last years' review (**Table 2**). Differences are due to corn variety and also, but in a lesser way, extraction method. Anthocyanin composition in cob is similar to the kernel, finding the six main anthocyanins, and identification has made by HPLS-MS [15, 40].

2.3. Anthocyanin in pigmented corn silk

Corn silk can be yellow, green or purple depending on the corn variety. Silk is used in local community as medicinal herbs; however, it does not take advantage and is considered a waste [34].

Part of the corn	Corn phenotype	Anthocyanin	Ref.
Kernel	Purple corn[2] Purple corn bran[3] Purple corn pericarp[6]	Cy-3-glu (45.8%)[2], (45.8%)[3], (47.3%)[4] (73.62%)[6] Pg-3-gluc (2.0%)[2] (3.3%)[3], (4.7%)[4] (15.50%)[6] Pn-3-gluc (9.3%)[2], (4.,1%)[3], (11.9%)[4] (10.88%)[6] Cy-3-malonylglu (17.2%)[2], (11.9%)[4] Pg-3-malonylglu (2.4%)[2], (2.1%)[4] Pn-3-malonylglu (3.1%)[2], (6.0%)[4] Condensed form (16.8%)[2], (11.2%)[4]	[11][4], [12][2], [13][3]
	Purple corn V1-V9[1] Purple corn[2,3,9] Purple Hybrid (WenveiiR5 R11)[5]	Condensed forms[1]; Cy-3-glu[1,2,3,5,6], Pg-3-gluc[1,2,6,9]; Pn-3-gluc[1,2,5,6,9]; Cy-3-malonylglu[1,2,3,5]; Pg-3-malonylglu[1,2,3,5]; Cy-3-dimalonylglu[1]; Pn-3-malonylglu[1,2,3]; Pg-3-dimalonylglu[1,2]; Pn-3-dimalonylglu[1]	[9][5], [10][1], [12][2], [14][6], [15][9]
	Red hybrid corn (Wenwei2 R6 x LH287 R8)[5]	Cy-3-glu[5]; Pn-3-gluc[5]; Cy-3-malonylglu[5]	[9][5]
	Blue corn	Cy-3-glu (24.4%)[7] (61.50%)[8] Pg-3-glu (13.88%)[8] Pn-3-glu (3.39%)[8] Cy-3-malonylglu (56.6%)[7] Pg-3-malonylglu (9.1%)[7] Pn-3-malonylglu (10.4%)[7] Cy-3-succinylglu (3.62%)[8] Cy-3-disuccinylglu (4.56%)[8]	[11][7], [16][8]
	Blue hybrid corn (Lfy blue RI)[5]	Cy-3-glu[5]; Cy-3-malonylglu[5]; Pn-3-malonylglu[5]	[9][5]
Germ	Purple corn sprouts	Direct condensed (Epi)catechin-Cy/Pg-3,5 diglu (Epi)catechin (4-8)-Cy/Pn/Pg 3,5 diglu (Epi)catechin (4-8)-Cy 3-malonylglu-5 glu Cy- 3,5 diglu Cy/Pg/Dp/Pn 3-glu Cy 3-malonylhexoside Cy/Pg/Pn 3-(6″-malonylglu) Pn-3-(6″-malonylhexoside) Cy/Pg/Pn 3-(3″,6″-dimalonylhexoside)	[17]
Cob	Purple corn[9] Purple corn (Peru)[10]	Cy-3-glu[9, 10]; Cy-3-malonylglu[9, 10]; Pn-3-glu[9, 10]; Pn-3-malonylglu[9, 10]; Pg-3-glu[9, 10]; Pg-3-malonylglu[9, 10]	[15][9], [18][10]
	Purple corn (Peru)	Cy-3-glu (75.28%) Pn-3-glu (8.55%) Pg-3-glu (16.16%)	[14]

Part of the corn	Corn phenotype	Anthocyanin	Ref.
Husk	Purple corn	Cy-3-glu (11.7%)[11] (39.8%)[12] Cy-3-malonylglu (29.0%)[11] (8.4%)[12] Pg-3-malonylglu (11.0%)[12] Cy-3-succinylglu (20.8%)[12] Cy-3-glu monomalonate (1.0%)[11] Pg-3-glu (~1.5%)[11] (2.0%)[12] Cy-3-malonylglu (6.3%)[11] Pn-3-glu (0.9%)[11] Cy-3-glu dimalonate (3.9%)[11] Cy-3-dimalonylglu (35%)[11] Pn-3-malonylglu (2.0%)[11] Pg-3-dimalonylglu (1.5%)[11] Pn-3-dimalonylglu (1.4%)[11]	[19][11], [20][12]
Silk	Purple corn	Cy-3-glu Cy-3-malonylglu Pg-3-glu Pn-3-glu	[21]

Superscript indicates the correlation of the concentration of anthocyanins with its reference.

Table 1. Composition of Anthocyanins found in pigmented corn plant.

Part of corn	Maize phenotype	Extraction method	Anthocyanins content (mg/100 g)	Ref.
Maceration				
Kernel	Purple/Blue (*Zea mays var. saccharata*)	Heat water 60 min	878.9/26.2	[22]
Kernel	Purple Corn	2% formic acid, 2 h 40:1 liquid-to-solid 3 extractions	473	[11]
Kernel	Purple (AREQ-084)	Alcoholic extraction (Methanol or ethanol) with acid (85:15 v/v) 1–3 extractions	310	[23]
	Purple (*Zea mays* L., cv Zihei)		55.8	[15]
	Purple (AREQ-516540TL)		850	[24]
	Purple (EP24)		153	[25]
	Purple (race Conico)		97–426	[26]
	Purple corn		1600	[27]
	Purple (KKU-WX)		74.5	[28]
	Purple corn (ZM01-ZM22)		0.8–111.7	[29]
Kernel	Red corn (ZM01-ZM22)	Methanol acid	0.8–33.4	[29]

Part of corn	Maize phenotype	Extraction method	Anthocyanins content (mg/100 g)	Ref.
Kernel	Pink (ZM01-ZM22)	Methanol acid	0.3–1.4	[29]
	Pink (EP24)		0.018	[25]
Kernel	Blue pericarp	Alcoholic extraction (Methanol or ethanol) with acid (85:15 v/v) One to three extractions	39	[11]
	Blue (ZM01-ZM22)		7.3–7.4	[29]
	Blue (race Chalqueño)		64.6	[30]
	Blue (race Conico)		89.2	[30]
	Blue hybrid corn		73.0–105.2	[30]
	Blue hybrid corn		27.39–78.28	[31]
Cob	Red/Purple waxy corn **1.** KKU-WX111031 **2.** KKU-OP **3.** hybrid **4.** commercial	Methanol-1% citric acid (80:20 v/v) Mixed 24 h, 4°C	**1.** 34/37 **2.** 116/179 **3.** 17/189 **4.** 27/336	[5]
Cob	Purple waxy corn (red to black)	Methanol Shaken for 2 h 1:10 Two extractions	202–1423	[32]
Cob	Purple hybrid corn (KPSC 901)	Conventional heating	3660	[33]
		Microwave	3970	
		Ultrasound	3830	
		Ohmic heating	3280	
Husk	Purple corn husk	0.1 N HCl 6 h, room temperature	3500	[19]
Husk	Red/Purple waxy corn **1.** KKU-WX111031 **2.** KKU-OP **3.** hybrid **4.** commercial	Methanol-1% citric acid (80:20 v/v) Mixed 24 h, 4°C	**1.** 5/3 **2.** 34/130 **3.** 48/494 **4.** 5/213	[5]
Silk	Purple (ZPEXP)/Pink (ZP341) Purple hybrid (PWC1-5)	Methanol acidified with 1 N (85:15 v/v) Shaking by 30 min 70°C, 1.5 h	193/1.49 0.44–2.38	[34, 35]
Silk	Purple corn	Ethanol 50% Ratio 1:1 w/v 5 min	970	[21]

Part of corn	Maize phenotype	Extraction method	Anthocyanins content (mg/100 g)	Ref.
Silk	Red/Purple waxy corn **1.** KKU-WX111031 **2.** KKU-OP **3.** hybrid **4.** commercial	Methanol-1% citric acid (80:20 v/v) Mixed 24 h, 4°C	**1.** 78/478 **2.** 408/419 **3.** 289/456 **4.** 249/500	[5]
Germinated	Purple corn (PMW-581)		240	[17]
Foliar	Purple corn (Jingzi No. 1)	Ethanol 60% with citric acid 1% 60°C, 120 min	1780	[36]
Ultrasound assisted extraction				
Kernel	Purple corn	96% ethanol and 1.5 N HCl (85:15) 1:25/80 solid-to solvent 15 min Two extractions	10–300 (kernel) 70–3700 (pericarp)	[8]
Kernel	Purple corn bran	400 W	362	[13]
Cob	Dried cob of purple waxy	65°C, 35 min 1:20 solid-solvent ratio	2.4	[37]
Supercritical fluid technology				
Kernel	Purple corn pericarp (Peru)	50°C, 400 bar Supercritical CO2→Ethanol→H_2O	1060	[14]
Kernel	Purple waxy corn (*Zea mays* L. var. ceratina)	Subcritical solvent extraction method Water-ethanol 1:3 Sample-to-solvent ratio 1:20)	99	[38]
Cob	Purple waxy corn (*Zea mays* L. var. ceratina) Peru	Subcritical solvent extraction method Water-ethanol 1:1 Sample-to-solvent ratio 1:20)	1240–1270	[14, 38]
Silk	Purple waxy corn (*Zea mays* L. var. ceratina)	Subcritical solvent extraction method Water-ethanol 1:1 Sample-to-solvent ratio 1:30)	1550	[38]
Kernel	Purple waxy corn *Zea mays L. ceratina*	High-pressure processing 700 MPa (30–45 min)	116	[39]

Table 2. Anthocyanins extraction methods and concentration.

But silk has a great potential to obtain phenolic compound, among them, anthocyanins. Research of silk is about its quantification and characterization of anthocyanins and results showed that has the highest anthocyanins concentration of the whole plant [41].

2.4. Anthocyanin in pigmented corn husk

Husk is the least studied part of the corn; there is limited research about their anthocyanin composition; however, they had a high concentration of anthocyanins depending on corn variety [20]. Most recent reports show a deeper studied of the type of anthocyanins in purple husk which has more anthocyanin diacylated [19] but there is other report that found cyaniding-3-succinylglucoside instead of diacylated anthocyanin [20]. For that reason, more research is needed; due to the low information, it is not possible to ensure that corn husk composition is different from other parts.

2.5. Extraction methods and characterization of anthocyanins in pigmented corn

Extraction of anthocyanin is made with methanol solvent acid and the method most used is ultrasound-assisted extraction that shows better efficiency, although, microwave-assisted extraction, ohmic heating extraction and supercritical solvent extraction are also used. Liquid chromatography techniques are the most used in anthocyanin identification. **Table 2** shows the extraction methods used until 2018 and the anthocyanin content.

2.6. Biological activity of pigmented corn anthocyanins

Structural anthocyanins have conjugation that provides stabilization of free radicals. Antioxidant activity is plenty reported in pigmented corn. Additionally, anthocyanin extract of pigmented corn has been used in *in vitro* and *in vivo* assays, **Table 3** shows some of the activities studied where anti-obesity is the most recurrent.

Extract of anthocyanin	Biological activity		Ref.
Red corn	Inhibition proliferation of colorectal cancer cell	*In vitro* Cell lines	[42]
Purple corn	Inhibition proliferation of colorectal cancer cell	*In vitro* Cell lines	[42]
Purple corn (hybrid maize) kernel	Cardioprotective activity	In vitro	[43]
Purple maize flour	Reduce visceral adiposity index, total body fat mass, systolic blood pressure, total cholesterol and plasma triglycerides. Improve glucose tolerance, liver and cardiovascular structure and function	*In vivo* In rats diet	[44]
Purple corn pericarp	Adipogenesis, inflammation and insulin resistance in adipocytes	*In vitro*	[45]
Purple waxy corn cob	Neuroprotective and memory enhancing effect		[46]
Purple corn silk (*Zea mays* L. var. ceratina)	Anti-obesity agent		[21]
Blue tortillas	Learning capability	In rats diet	[47]

Table 3. Biological activity found in purple corn.

2.7. Applications of pigmented corn anthocyanins

Purple corn is used traditionally to make tortillas, atole, chips, popcorn and other type of food products. However, chemical studies of these food products are limited. Food industry is more interested in elaboration of products with a major quality and bioactive compounds content; in consequence, the development of new products with purple corn have been the most studied. Some of the developed products are presented in **Table 4**, where the main purpose was to find the best process to keep the major anthocyanins concentration.

Additionally, the anthocyanins are used to make photosensitizers from different colored parts of the corn including cob, husk and silk.

Furthermore, due to the low stability of anthocyanins, there are some studies related to this topic. The stability of anthocyanins has been improved using intermolecular copigmentation with gallic ferulic, caffeic acids, and results show that those acids do not protect the anthocyanins only have a hypochromic effect. There is a better protection by self-association. Other strategy is the encapsulated of anthocyanins in alginate-pectin hydrogel [49] and the spray-dried purple corn found that 5% of maltodextrin, 150°C and water are the best condition to obtain a soluble product with the major anthocyanin concentration [50]. Haggard in 2018 also found that beverage with more pelargonidin-3-glucoside concentration has a major half-life [10].

Corn phenotype	Use	Ref.
Purple corn	Beverage	[12]
Blue popping corn and dark-red popping corn (*Zea mays* L. spp. Everta)	Bakery (cookies) with higher phenolic content	[4, 35]
Purple corn (husk, cob and silk)	Photosensitizers	[48]

Table 4. Use of anthocyanins found in pigmented corn.

3. Phenolic acids in pigmented corn

Pigmented corns are good source of phenolic acids; mainly hydroxycinnamic acids but also hydroxybenzoic and chlorogenic acids. These compounds are distributed in whole plant. **Table 4** shows the main phenolic acids found in different parts of the plant reported in the literature (**Figure 5**).

In white, yellow and pigmented maize, ferulic acid is the most abundant phenolic acid. There are reports that in white and yellow corn it can be found in the forms of dimers, trimers and tetramers [51]. Other authors have reported 1.94 mg/100 g [52] of free diferulic acid in blue Mexican corn which is the most abundant in that variety (**Table 5**).

3.1. Phenolic acid in pigmented corn kernel

Free ferulic acid concentration in a variety of pigmented kernel is similar among Mexican and Khao Niew Dum varieties (2.02–3.99 mg/100 g) [24, 52]; however, Peruvian variety has the highest concentration with 5.50 mg/100 g [53].

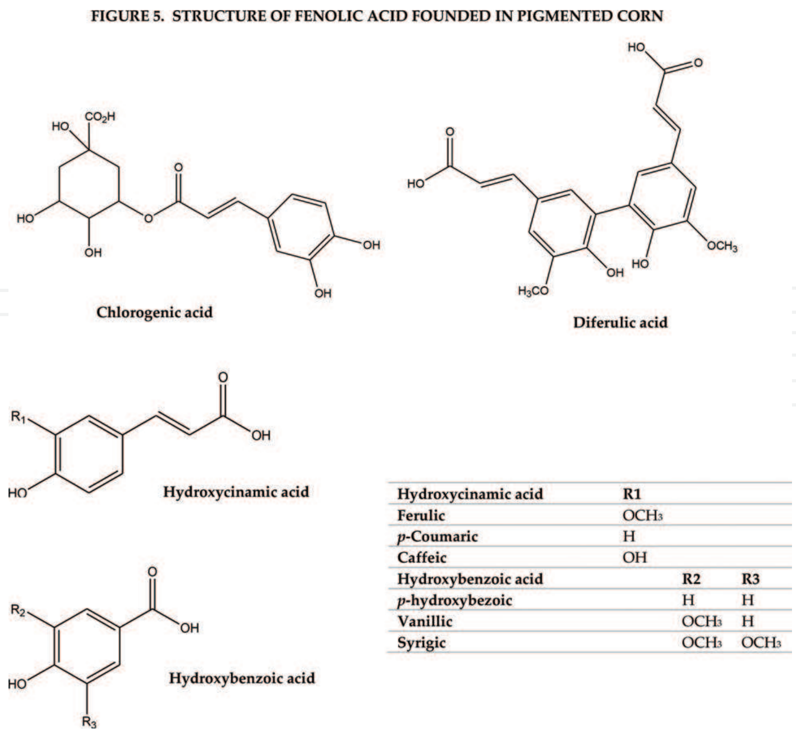


Figure 5. Phenolic acids structures in pigmented corn.

Corn part	Phenolic acid	Pigmented corn phenotype	Content (mg/100 g)	Ref.
Kernel	Ferulic acid	Peruvian purple (INIA-GOI)	5.52	[53]
		Mexican pigmented Pigmentados	1.97–2.02	[24]
		Blue-Queretaro (Mexico)	1.94	[52]
		Purple corn variety Khao Niew Dum	2.3	[54]
Kernel	*p*-Coumaric acid	Blue-Queretaro (Mexico)	0.512	[52]
		Purple corn variety Khao Niew Dum	1.1	[54]
Kernel	Diferulic acid	Blue-Queretaro (Mexico)	1.9	[52]
Kernel	Caffeic acid	Peruvian purple (INIA-GOI)	3.81	[53]
		Purple corn variety Khao Niew Dum	0.29	[54]
Kernel	*p*-Hydroxybenzoic acid	Purple corn variety Khao Niew Dum	0.18	[54]
Kernel	Vanillic acid	Purple corn variety Khao Niew Dum	0.98	[54]
Kernel	Chlorogenic acid	Peruvian purple (INIA-GOI)	1.05	[53]
Silk		Silk from Thai purple corn	25.64	[21]
Cob	Syringic acid	Purple corn cob from four phenotypes of Thai corn	31–202.78	[32]

Table 5. Free phenolic acid concentration in different phenotypes of pigmented corns.

Also, there are reports that evaluate ferulic concentration among different Mexican corn phenotypes pigmented white and yellow and there are no statistically significant differences. The concentration is between 140 and 160 mg and 94–98% are bounded in cell wall and the rest is free [24]. In the cell wall, ferulic acid plays an important role because it is cross-linked through photochemical reactions or coupling reactions catalyzed by peroxidases with the polysaccharides present in the grains, thus improving the rigidity in the cell wall of corn [51].

Other acids found in pigmented maize kernel are as follows: *p*-coumaric, caffeic, vanillic, chlorogenic and hydroxybenzoic acids, however concentrations are different according to the variety. In purple maize variety Khao Niew Dum, the next acid apart of the ferulic acid are *p*-coumaric, vanillic, caffeic and *p*-hydroxybenzoic acid [54]; while in INIA-GUI purple corn from Peru, the acid with major concentration after ferulic acid is the caffeic acid and cholorogenic acid [53]. The difference in concentration could depend on different factors as genetic, environmental, ripening, light-UV exposure and insect and pathogens attack [51].

3.2. Phenolic acid in pigmented corn cob

Research about pigmented corn cob is low; nevertheless, they have concentrations of important phenolic acids. The most abundant phenolic acid in cob from four pigmented corn phenotypes is syringic acid (31–202.78 mg/100 g) [32], followed by ferulic acid (7.34–10.73 mg/100 g) and in minors amounts vanillic acid (1.42–7.05 mg/100 g) and hydroxybenzoic acid (0.73–7.05 mg/100 g).

3.3. Phenolic acid in pigmented corn silk

Other organ from maize plant which has been studied due to their higher concentration of phenolic acids, in particular chlorogenic acids, is the stigma, commonly called silk. Some authors highlight that silk from purple corn have 25.64 mg/100 g of chlorogenic acid [21] and other studies highlight that from 25 days after emergence from four phenotypes of corn (purple, green, pink and yellow) they have 21.2–29.3 mg/100 g of 3-caffeoylquinic acid, and 5 days after emergence 923.7–1840.8 mg/100 g [37], also other three chlorogenic acids where studied: 4-caffeoylquinic acid (186.9–362.1 mg/100 g), 5-caffeoylquinic acid (74.4–86.5 mg/100 g) and *p*-coumaroylquinic acid (43.4–90.9 mg/100 g). Purple and green silk has the major concentration of chlorogenic acids.

3.4. Extraction methods and characterization of phenolic acids in pigmented corn

As already mentioned, most of the phenolic acids in the corn kernel are bound to the cell wall and a minimum amount are free form; for this reason, the way to extract them to identify and quantify them is not simple and is diverse: some authors point to the extraction of free phenolic acids, making an extraction with 80% methanol and centrifuging [31]; while the solid of the methanol extraction was carried out by a basic hydrolysis (with NaOH) with a water bath at 80°C for 30 min, and in this way the acids bound to the cell wall are obtained. Other authors report successive extraction methods for the recovery of free and bound phenolic acids; first for the free acids, they performed an extraction with 80% ethanol using a high-performance disperser, then the residue was assisted by adding an enzyme cocktail (pectinases, amylases and cellulases). To the residue of this, they made a thermal hydrolysis doing another extraction with methanol and 70°C. Finally, to the solid residue of this extraction, they added NaOH to carry out a basic hydrolysis [55].

In the case of phenolic acids present in corn silk, they only report extractions with organic solvents; for example, performing a direct extraction of the silk, using 95% methanol, centrifuging and using the supernatant for quantification and characterization [35]; other studies use 50% ethanol [21]. In the same way, for the case of the phenolic acids of the cob where they describe a simple extraction using methanol and centrifugation [32].

To carry out the characterization and quantification of each of the phenolic acids perform chromatography techniques: such as HPLC and HPLC-MS [52–55].

3.5. Biological activity of pigmented corn phenolic acids

The phenolic acids present in the pigmented corns are of great importance due to the biological effects on human health [56], such as anticancer properties, antimutagenic, anti-inflammatory and cardiovascular diseases [56]. **Table 6** shows the biological properties of each of the phenolic acids present in the pigmented corn plant.

The biological activity that most report is as antioxidant, with phenolic acids having the capacity to reduce the free radical formation and elimination of ROS, inhibition and repair of lesions caused by the oxidation and degradation of other molecules and biomolecules [57].

Phenolic acid	Biological activity	Ref.
Ferulic acid	Potential antioxidant	[24, 52]
	Anticancer properties	[57]
	Against cardiovascular diseases	[56]
Coumaric acid	Reduction of blood glucose	[21]
Diferulic acid	Potential antioxidant Allelopathic effects	[52]
Caffeic acid	Immunostimulatory properties	[58]
p-Hydroxybenzoic acid	Immunostimulatory properties	[58]
Vanillic acid	Reduction of blood glucose	[21]
Chlorogenic acid	Potential antioxidant	[58]
	Reduce visceral adiposity index	[21, 35]
Syringic acid	Effect against cerebral ischemia Antihypertensive	[32]

Table 6. Phenolic acids present in pigmented maize and their biological properties.

The effect of antioxidant activity on corn from Bajio and Morelos (Mexico) has been evaluated; wherein the amount of free and bound phenols was measured; concluding that the antioxidant activity increases three times more in the extractions with basic hydrolysis. Therefore, antioxidant increase is attributed to phenolic acids linked mainly to phenolic acid [31]. In other studies, they reported that one-third of the antioxidant activity of the phenolic fraction in Mexican pigmented corn is given by ferulic acid [24]. They have also described the antioxidant activity between phenolic compounds, reporting that the highest antioxidant activity is generally presented by hydroxycinnamic acids, with ferulic acid presenting the highest and hydroxybenzoic acids less activity. In the case of purple and pink corn silk [35], high antioxidant activity is attributed mainly to chlorogenic acids, these activities being so high that they could be compared with other medicinal plants such as *Mentha piperita* and *Salvia officinalis*.

4. Flavonoids in pigmented corn

Other import group of the bioactive compounds that contain the pigmented corns are of flavonoids; with>4000 compounds, these molecules are most abundant polyphenols present in plant foods. They are characterized by a 15-carbon skeleton, organized as C6-C3-C6, with different substitutions making up the different subclasses. The major groups of the flavonoids of nutritional interest are the flavonols or catechins [59].

The most common chemical structures of flavonoids in corn are shown in **Figure 6**, and the composition of flavonoids in different parts of is presented in **Table 7**.

4.1. Flavonoids in pigmented corn kernel

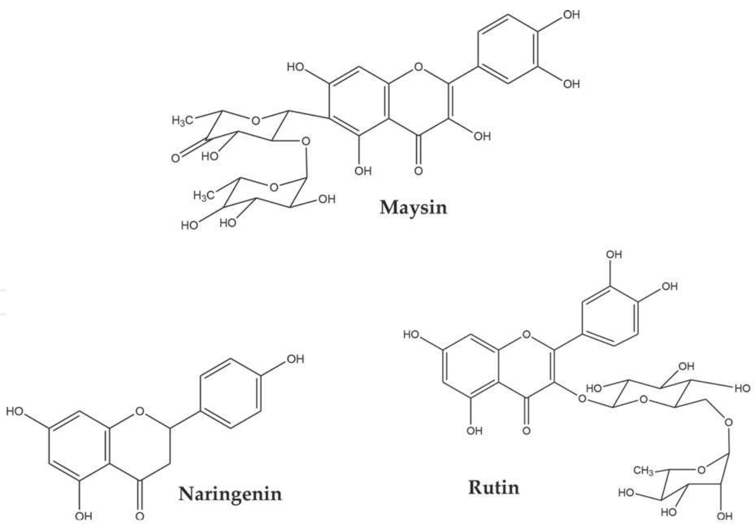
Peruvian purple corn has kaempferol and morin as major flavonoids in kernel (**Table 8**), the concentration is 202–224 mg/100 g [53] which represent almost the total flavonoids (**Table 9**); after kaempferol and morin the naringenin glucoside and in minor amount rutin and quercetin. Meanwhile, Serbian pigmented corn phenotypes [35] report a lower total flavonoid concentration with 19.90–33.75 mg/100 g.

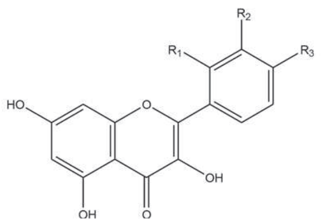
4.2. Flavonoids in pigmented corn silk

Flavonoids are the main bioactive compounds in pigmented corn silk [35] as shown in **Table 9**. Some authors reports until 3644.9 mg/100 g in Serbian purple corn and Mexican pigmented corn reports 797.1 a 2602.4 mg/100 g [61]. Among the flavonoids identified and quantified in pigmented corn silk is the maysin with 12.6–17.1 mg/100 g [35], quercetin (1.58 mg/100 g) and narigenin glucoside (6.45 mg/100) [21].

4.3. Flavonoids in pigmented corn pollen

Other organ of pigmented corn (blue, red and red dark) which represent higher concentration of total flavonoids is pollen (916.36–1087.69 mg/100 g) **Table 9**. The flavonoids identified are (**Table 8**) hyperoside, rutin and quercetin [60].





Flavonoid	R1	R2	R3
Quercetin	H	OH	OH
Morin	OH	H	OH
Kaempferol	H	H	OH

Figure 6. Flavonoids structures in pigmented corn.

Flavonoid	Part of corn	Pigmented corn phenotype	Total flavonoid content (mg/100 g)	Ref.
Quercetin	Silk	Thai purple corn silk	20.26	[21]
	Pollen	Red corn	0.111	[60]
		Blue corn	0.569	
		Dark red corn	0.145	
	Kernel	Peruvian purple corn	1.58	[53]
Naringenin glucoside	Silk	Thai purple corn silk	6.45	[21]
	Kernel	Peruvian purple corn	14.8	[53]
Maysin	Silk	Serbian purple corn	17.1	[35]
		Serbien pink corn	12.6	
Rutin	Pollen	Red corn	0.186	[60]
		Blue corn	0.013	
		Dark red corn	0.010	
	Kernel	Peruvian purple corn	2.74	[53]
Hyperoside	Pollen	Red corn	0.897	[60]
		Blue corn	0.655	
		Dark red corn	0.537	
Kaempferol	Kernel	Peruvian purple corn	224.0	[53]
Morin	Kernel	Peruvian purple corn	202.0	[53]

Table 7. Flavonoid concentration in different parts of pigmented corn.

Parts of the corn	Pigmented corn phenotype	Total flavonoid concentration (mg/100 g)	Ref.
Silk	Serbian purple corn	3644.9	[35]
	Serbian pink corn	3594.2	
	Mexican red corn	2602.4	[61]
	Mexican dark red corn	797.1	
	Mexican white-purple corn	809.5	
Pollen	Red corn	1087.69	[60]
	Blue corn	916.36	
	Dark-red corn	1056.21	
Kernel	Peruvian purple corn	261–266	[53]
	Red	26.76	[62]
	Dark red	27.05	
	Red-yellow	26.84	
	Light blue	33.75	
	Dark blue	30.74	
	Multicolor	19.90	
Corn	Peruvian purple corn	187	[14]
Pericarp	Peruvian purple corn	4200	[14]

Table 8. Total flavonoid concentration in different parts of pigmented corn.

4.4. Extraction methods and characterization of flavonoids in pigmented corn

Flavonoid extraction methods in pigmented corn are made using simple extraction using organic solvents (methanol, ethanol and water in different proportions), centrifuge and using aqueous solution for analysis [21, 35, 53, 60].

Characterization and quantification of each one is made by chromatography techniques as HPLC and HPLC-MS [21, 53].

Flavonoids	Biological activity	Ref.
Quercetine	Apoptosis induction	[18]
	Adiposites lipolysis	
	Antioxidant activity	[56]
Naringenin glucoside	Antioxidant activity	[50]
Maysin	Neuroprotector	[31]
Rutin	Antioxidant activity	[56]
Hyperoside	Antioxidant activity	[56]
Kaempferol	Antioxidant activity	[50]
Morin	Antioxidant activity	[50]

Table 9. Biological activity of maizes flavonoids.

4.5. Biological activity of pigmented corn flavonoids

The most important biological activities of flavonoids in pigmented corns that are reported in the last 10 years are presented in **Table 9**.

Flavonoids of pigmented corns have been studied mainly for their antioxidant and neuroprotection activities. Corn flavonoids have also been reported, which can act as inductors of apoptosis and lipolysis of adipocytes.

5. Conclusions

Pigmented corns and its parts is a food that can be beneficial to the human because of the presence of phytochemicals and biological activities that are present. The studies of pigmented corns have been increased year after year, and they showed that the coloration blue, purple, pink and red is given by anthocyanins. Also, they have a large amount of phenolic acids and flavonoids. These compounds are present in the whole plant (kernel, cob, husk, silk), and their concentration is different depending on the organ.

The most abundant anthocyanins in corn plant are cyanidin-3-glucoside, cyanidin-3- (6″-malonyl) glucoside, peonidin-3-glucoside, peonidin-3- (6″-malonyl) glucoside, pelargonidin-3-glucoside and pelargonidin-3-(6″malonyl) glucoside and the coloration of each corn is depending on the concentration and profile of these.

With reference to phenolic acids, the representatives are ferulic acid in the kernel, syringic acid in the cob and chlorogenic acid in the silk. Finally, the flavonoids are morin, kaempferol, naringin, maysin, rutin, quercetin and hyperoside; the concentrations of these compounds are high especially in purple silk. Each of these compounds has a biological activity, so in the case of anthocyanins is its anti-cancer activity, cardioprotective and anti-obesity activity; according to phenolic acids, the ferulic acid is a potential antioxidant and provides anticancer properties, and in general, flavonoids have antioxidant activity.

Therefore, pigmented corns are important for the development of new functional food products from the grain and for obtaining natural colorants and antioxidants from the other parts of the plant.

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